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(54) Title: HERBICIDAL EMULSIFIABLE CONCENTRATES

(57) Abstract: The invention relates to a non-aqueous, emulsifiable concentrate (EC) formulation for herbicidal crop protection active compounds which consists essentially of: a) 25 to 150 g/L of at least one fluorinated herbicidal compound; b) 400 to 900 g/L of one or more herbicidal alkyl phenoxyalkanoates; c) 10 to 100 g/L of at least one non-ionic surfactant; d) 10 to 100 g/L of at least one benzene sulfonate; e) 50 to 600 g/L of one or more solvent selected from the group consisting of aliphatic or aromatic hydrocarbons, methylated plant oils and water-miscible polar aprotic organic solvents; and f) optionally, up to 5 g/L of at least one defoamer; and to the use of such an emulsifiable concentrate as a herbicide.



**WO 01/01777 A1**

## HERBICIDAL EMULSIFIABLE CONCENTRATES

### BACKGROUND OF THE INVENTION

Emulsifiable concentrate (EC) formulations are favored liquid delivery systems for agriculturally active compounds. As a rule, conventional ECs contain an active ingredient, one or more surfactants  
5 which act as emulsifiers upon dilution of the EC with water, and a water immiscible solvent. Typical solvents for conventional EC formulations are aliphatic or aromatic hydrocarbons, as for example, xylene, Shellsol A or Solvesso 200. These solvents have very low solubilities in water and are capable of dissolving a wide range of active ingredients.

10 Due to the presence of the solvent, many pesticides formulated as an EC have advantages such as a higher degree of systemicity and higher overall activity compared to the same pesticide formulated as a wettable powder (WP), water dispersible granule (WG) or suspension concentrate (SC).

15 Such concentrates are easy to store and transport and various adjuvants may be added to increase the efficacy of the formulation. A good EC, however, requires that a stable emulsion is formed upon dilution with water, which emulsion does not separate upon standing. Furthermore, there should not be any crystallization of the active from the  
20 EC after water dilution. In addition, the EC itself has to be physico-chemically stable during extended storage periods and under widely varying storage temperatures.

International Patent Application WO 98/48624 suggests the improvement of the emulsion stability of ECs containing low amounts of a  
25 water-insoluble fluorinated active agricultural ingredients which optionally contains a diluent active agricultural ingredient, by using a comparably

high amount of a water-insoluble C<sub>6</sub>-C<sub>18</sub> alkyl pyrrolidone. However, the C<sub>6</sub>-C<sub>18</sub> alkyl pyrrolidones are highly corrosive and too expensive to be used in a broad range herbicidal product for common use.

Moreover, WO 98/48624, preferably uses an ethoxylated nonyl  
5 phenol phosphate ester as an anionic surfactant. These surfactants may damage the environment due to their capability to form toxic metabolites and their use is not favored due to their suspected estrogenic activity.

Accordingly, it is an object of the present invention to provide novel, herbicidal ECs.

10 It is a further object of this invention to provide a stable, effective emulsifiable concentrate (EC) containing low amounts of at least one fluorinated herbicidal compound with high amounts of one or more herbicidal alkyl phenoxyacetates acting as a diluent which do not have the disadvantages of the ECs of the art.

15 It is also an object of the invention to provide methods for controlling undesired weed by contacting plants with a herbicidally effective amount of these EC formations upon dilution with water.

It is another object of the invention to provide selective herbicidal compositions obtainable by emulsifying the new ECs in water.

20 These and other objects and features of the invention will be more apparent from the detailed description set forth hereinbelow, and from the appended claims.

### SUMMARY OF THE INVENTION

25

The present invention provides a novel stable, non-aqueous emulsifiable concentrate (EC) for herbicidally active compounds which consists essentially of

- (a) 25 to 150 g/L of at least one fluorinated herbicidal compound,
- 30 (b) 400 to 900 g/L of one or more herbicidal alkyl phenoxyalkanoates,
- (c) 10 to 100 g/L of at least one non-ionic surfactant,

- (d) 10 to 100 g/L of at least one benzene sulfonate,
- (e) 50 to 600 g/L of one or more solvents selected from the group consisting of aliphatic or aromatic hydrocarbons, methylated plant oils and water-miscible polar aprotic organic solvents, and
- 5 (f) optionally, up to 5 g/L of at least one defoamer:

These new emulsifiable concentrate formulations exhibit excellent selective herbicidal activity in various crops.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

10

It has surprisingly been found that the EC formulations consisting essentially of

- (a) 25 to 150 g/L of at least one fluorinated herbicidal compound,
  - (b) 400 to 900 g/L of one or more herbicidal alkyl phenoxyalkanoates,
  - 15 (c) 10 to 100 g/L of at least one non-ionic surfactant,
  - (d) 10 to 100 g/L of at least one benzene sulfonate,
  - (e) 50 to 600 g/L of one or more solvent selected from the group consisting of aliphatic or aromatic hydrocarbons, methylated plant oils and water-miscible polar aprotic organic solvents, and
  - 20 (f) optionally, up to 5 g/L of at least one defoamer;
- exhibit high physicochemical stability and excellent application properties.

As used herein in the new EC formulations, a "herbicidal compound" is a synthetic compound which has the capability of control undesired weeds in crops; and a "fluorinated herbicidal compound" is a  
25 synthetic compound which is substituted by at least one fluorine atom which has the capability of control undesired weeds in crops.

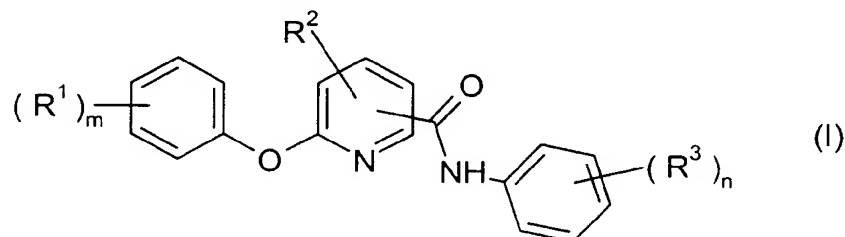
Suitable fluorinated herbicidal compounds are those which are solid at room temperature and are substantially insoluble in water, but soluble in an organic solvent.

30 Preferred fluorinated herbicides (a) are the compounds selected from the group consisting of:

acifluorfen, carfentrazone-ethyl, clodinafop-propargyl, diflufenican, dithiopyr, ethoxyfen-ethyl, flamprop-M-isopropyl, flamprop-M-methyl, flazasulfuron, fluazifop, fluchloralin, flufenacet (BAY FOE 5043 or fluthiamid), flumetsulam, flumioxazin, fluometuron, fluoroglycofen, flupoxam, fluridone, fluroxypyr, flurprimidol, flurtamone, fluthiacet-methyl, fomesafen, haloxyfop, isoxaflutole, lactofen, norflurazon, oxyfluorfen, picolinafen, propachlor, sulfentrazone, thiazopyr and trifluralin.

Most of these herbicidal compounds are described in "The Pesticide Manual," 11th Edition, The British Crop Protection Council and The Royal Society of Chemistry, 1997, (hereinafter abbreviated as "Pesticide Manual").

Preferred for use in the present invention are the fluorinated herbicidal compounds of formula I

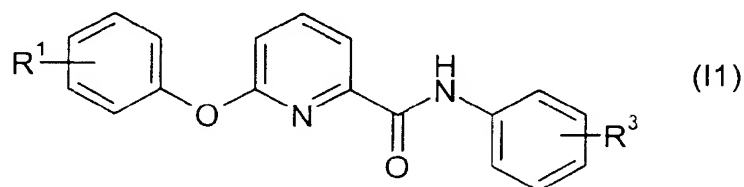


in which

$R^1$  and  $R^3$  each independently represent a fluorine atom or a fluoroalkyl, preferably a  $C_1$ - $C_6$  fluoroalkyl group, in particular a trifluoromethyl group;  $R^2$  represents a hydrogen atom or an optionally substituted alkyl or alkoxy group; and

$m$  and  $n$  each independently represent an integer from 1 to 2.

Particularly preferred herbicidal compounds (a) are the picolinamides disclosed by EP-A-0 447 004, in particular those of formula I1



wherein R<sup>1</sup> and R<sup>3</sup> are as described for formula I.

An especially preferred compound for use in the present invention is N-(4-fluorophenyl)-2-(3- $\alpha,\alpha,\alpha$ -trifluoromethylphenoxy)-6-pyridinecarboxamide, also known as picolinafen.

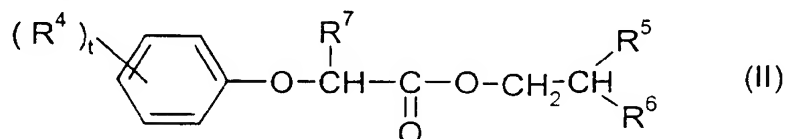
- 5 The new ECs contain at least one fluorinated herbicide (a) and at least one herbicidal alkyl phenoxyacetate (b).

The herbicidal compounds can be, for example, compounds which possess a high herbicidal activity within a wide concentration range and/or at low dosages, and may be used in agriculture, in particular, for the selective control of undesired plants such as *Alopecurus myosuroides*,  
 10 *Echinochloa crus-galli*, *Setaria viridis*, *Galium aparine*, *Stellaria media*, *Veronica persica*, *Lamium purpureum*, *Viola arvensis*, *Abutilon theophrasti*, *Ipomoea purpurea* and *Amaranthus retroflexus* by pre- and post-emergence application, particularly in certain crops such as maize  
 15 and rice.

Suitable herbicidal alkyl phenoxyalkanoates (b) are those which are liquid at room temperature and substantially insoluble in water, but soluble in an organic solvent.

Preferred alkyl phenoxyalkanoates are esters of 2-phenoxyacetic or  
 20 2-phenoxypropionic acid having a straight chained or branched C<sub>2</sub>-C<sub>12</sub> alkyl, in particular a branched C<sub>4</sub>-C<sub>10</sub> alkyl group. Most preferred are the 2-ethylhexyl esters.

Particularly preferred are the compounds of formula II



25 in which

R<sup>4</sup> each independently represents a halogen atom or a C<sub>1-6</sub> alkyl group,  
 R<sup>5</sup> and R<sup>6</sup> each independently represent a C<sub>1-6</sub> alkyl group,  
 R<sup>7</sup> represents a hydrogen atom or a methyl group, and

t represents an integer from 1 to 3.

Most preferred are the compounds selected from the group consisting of: 2-ethylhexyl (4-chloro-2-methylphenoxy)-acetate [also known as MCPA-2EH], 2-ethylhexyl (2,4-dichlorophenoxy)-acetate [also  
5 know as 2,4-D-2EH] and 2-ethylhexyl 2-(4-chloro-2-methylphenoxy) propionate [also known as mecoprop-2EH] or mixtures thereof.

Mixtures of the above mentioned herbicides or mixtures of herbicides with other active ingredients like fungicides, insecticides, acaricides and nematocides are possible.

10 Suitable non-ionic surfactants (c) are preferably polyglycolether derivatives of aliphatic alcohols and saturated or non-saturated fatty acids, which have 3 to 20 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon residue. Other suitable non-ionic surfactants are  
15 20 to 250 ethylene glycol ether groups containing polyadducts of ethylene oxide and propylene oxide, ethylene diamino polypropylene glycol and alkyl polypropylene glycol with 1 to 10 carbon atoms in the alkyl moiety. The substances normally contain 1 to 5 ethylene glycol units per propylene glycol unit. Examples of non-ionic surfactants are castor oil polyglycol ethers, polyadducts of ethylene oxide and propylene oxide,  
20 tributyl phenoxy polyethoxy ethanol and tristyrylphenol ethoxylates.

Preferred are ethoxylated oils such a castor or canola oil ethoxylates having at least 25, preferably 27 to 37 ethoxy units, such as Sunaptol® CA350 (castor oil ethoxylate with about 35 ethoxy units) of Uniqema (formerly ICI Surfactants), Mergital® EL33 (castor oil ethoxylate with  
25 about 33 ethoxy units) of Henkel KGaA, Eumulgin® CO3373 (canola oil ethoxylate with about 30 ethoxy units) of Henkel KGaA and Ukanil® 2507 (castor oil ethoxylate with about 32 ethoxy units) of Uniqema.

Another group of preferred nonionic surfactants (c) are alcohol alkoxylates, which are based on alkoxy units having 2 carbon atoms, thus  
30 being a mixed ethoxylate, or 2 and 3 carbon atoms, thus being a mixed

ethoxylate/propoxylate. In a preferred aliphatic alcohol alkoxylate, the alkoxylate chain may have at least 5 alkoxy moieties, suitably from 5 to 25 alkoxy moieties, preferably 5 to 15, in particular 5 to 11. The alcohol moiety is as a rule derived from a C<sub>9-18</sub> aliphatic alcohol. Preferred alcohols are typically 50 wt.-% straight-chained and 50 wt.-% branched alcohols.

Particularly preferred surfactants are the Synperonic® alcohol ethoxylates from Uniqema, in particular, Synperonic® 91-6.

Furthermore preferred alcohol alkoxylates are monobranched alcohol ethoxylates such as Atplus® MBA 11-7 (branched C<sub>11</sub> alcohol ethoxylate with 7 ethoxy units) of Uniqema or Genapol® X-60 (alcohol ethoxylate with 6 ethoxy units) of Clariant.

Suitable alkyl benzene sulfonates (d) are, for example, the sodium, calcium or triethyl ammonium salts of alkyl benzene sulfonic acid. Most preferred alkyl benzene sulfonates (d) are the sodium, calcium or triethyl ammonium salts of dodecyl benzene sulfonic acid, in particular Rhodacal® 70/B (70 % calcium dodecyl benzene sulfonate in n-butanol), Rhodacal® 60/BE (60 % calcium dodecyl benzene sulfonate in 2-ethylhexanol) and Rhodacal® 2283 (70 % ammonium dodecyl benzene sulfonate) all of Rhodia GmbH (formerly Rhône-Poulenc), Phenylsulfonat CA 100 (40 % calcium dodecyl benzene sulfonate in Genopol X-060 and Solvesso 200) of Clariant GmbH (formerly Hoechst AG) or Nansa® EVM 70/2E (57 % linear dodecyl benzene sulfonate in 2-ethylhexanol) of Albright & Wilson.

The surfactants (c) and (d) provide good emulsifying properties without containing alkylphenol ethoxylates, such as Synperonic® NP9 and/or the anionic derivatives thereof, for example, ethoxylated alkylaryl phosphate esters such as Rhodofac® RE 610. Alkylphenol ethoxylates and their derivatives may damage the environment due to their capability to forming toxic metabolites and their suspected estrogenic activity.



Suitable solvents (e) are non-polar water-immiscible solvents or polar aprotic water miscible organic solvents. The non-polar solvents are selected from the group consisting of aliphatic or aromatic hydrocarbons and esters of plant oils or mixtures thereof.

5 Aliphatic and aromatic hydrocarbons such as hexane, cyclohexane, benzene, toluene, xylene, mineral oil or kerosin or substituted naphthalenes, mixtures of mono- and polyalkylated aromatics are, for example, commercially available under the registered trademarks Solvesso®, Shellsol®, Petrol Spezial® and Exxsol®.

10 Esters of plant oils, which are used as nonpolar, water-immiscible solvents according to the present invention are, as a rule, alkyl esters obtainable from medium chained fatty acids by esterification with alkanols or by transesterification of the corresponding plant oils preferably in the presence of a lipase. Preferred fatty acids of these plant oils have 5 to 20,  
15 in particular 6 to 15 carbon atoms. In a preferred embodiment, the methyl ester of the plant oil used is the methyl ester of caprylic / capric ester or of capric ester having a distribution of fatty acid chain lengths around 10 units.

Particularly preferred methyl esters of plant oils are Witconol® 1095  
20 and Witconol® 2309 which are commercially available from the Witco Corporation, Houston, USA.

The water-miscible polar aprotic organic solvents are preferably compounds which exhibit a dielectric constant of 2.5 or more at 25° C, in particular from 2.7 to 4.0 at 25 °C. Particularly preferred are cyclic amides  
25 and lactones as for example N-methylpyrrolidone, N-cyclohexylpyrrolidone and  $\gamma$ -butyrolactone, most preferred are  $\gamma$ -butyrolactone and N-methylpyrrolidone or mixtures thereof.

Also preferred are water-miscible polar aprotic solvents selected from the group consisting of alkyl lactates, in particular, isopropyl lactate  
30 such as Plurasolv® IPL which is obtainable from Plurac, alkyl carbonates,

polyethylene glycols, polyethylene glycol alkyl ethers, polypropylene glycols and polypropylene glycol alkyl ethers, and most preferably particular isopropyl lactate, or mixtures thereof.

Suitable defoamers (f) are siloxan derivatives or

- 5 perfluoroalkylphosphonic / perfluoroalkylphosphinic acids, in particular polydimethylsiloxanes, such as Rhodorsil® 416 or Rhodosil® 454 from Rhodia or mixtures comprising perfluoro-(C<sub>6-18</sub>)-alkylphosphonic acids and perfluoro-(C<sub>6-18</sub>)-alkylphosphinic acids, such as Fluowet® PL80, Fluowet® PP from Clariant.

- 10 Preferred embodiments of the invention are EC formulations which consist essentially of:

- (a) 30 to 125 g/L, in particular 40 to 110 g/L, of at least one fluorinated herbicidal compound of formula I, in particular, a compound of formula I1, most preferred picolinafen;
- 15 (b) 700 to 875 g/L, in particular 750 to 850 g/L, of one or more herbicidal alkyl phenoxyalkanoates of formula II, most preferred 2,4-D-2EH, MCPA-2EH or mecoprop-2EH;
- (c) 20 to 75 g/L, in particular 40 to 70 g/L, of at least one non-ionic surfactant, in particular, of at least one ethoxylated castor oil;
- 20 (d) 20 to 75 g/L, in particular 40 to 70 g/L, of at least one sodium or calcium alkyl-benzene sulfonate;
- (e) 50 to 200 g/L, in particular 60 to 150 g/L, of one or more solvents selected from the group consisting of aliphatic or aromatic hydrocarbons, methyl C<sub>8-12</sub> carboxylates, N-methylpyrrolidone,  $\gamma$ -
- 25 butyrolactone and isopropyl lactate; and
- (f) optionally up to 2 g/L of at least one defoamer selected from the group consisting of polydimethylsiloxanes and perfluoroalkylphosphonic / perfluoroalkylphosphinic acids:

Another aspect of the invention is a process for the preparation of an EC as described hereinbefore, which comprises mixing all the components in a dissolver.

Furthermore, the invention relates to a method of combating pests at  
5 a locus which comprises treating the locus with a composition obtained from emulsifying an EC according to the invention in water. Moreover, the invention relates to the use of an EC according to the invention as a pesticide.

As commodities, the inventive pesticidal ECs of the present invention  
10 are preferably in a concentrated form whereas the end-user generally employs diluted compositions. Said compositions may be diluted to concentrations down to 0.001% of active ingredient (a.i.). The doses usually are in the range of about 0.01 to 10 kg a.i./ha.

The said compositions may also comprise other auxiliaries such as  
15 chemical stabilizers, viscosity controlling agents, thickeners, adhesives, fertilizers, or other active pesticide ingredients to obtain special effects.

The ECs according to this invention exhibit a high physicochemical stability despite the high concentrations of the herbicidally active ingredients (a) and (b). The emulsions obtained with these ECs upon  
20 dilution with water are surprisingly stable, although they do not contain any additional C<sub>6</sub>-C<sub>18</sub> alkyl pyrrolidones.

For a clearer understanding of the invention, specific examples are set forth below. These examples are merely illustrations and are not to be understood as limiting the scope and underlying principles of the invention  
25 in any way. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the following examples and foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

Preparation Examples

The registered trademarks and other designations denote the following products:

Ingredient	Composition	Manufacturer
AgsoEx® 1	N-methylpyrrolidone	ISP
AgsoEx® BLO	$\gamma$ -butyrolacton	ISP
Atlox® 4855B	Blend of calcium alkylarylsulfonate and nonionic surfactant in an aromatic solvent	Uniqema
Exxsol® D110	Aliphatic hydrocarbon mixture	Exxon Chemicals
Fluowet® PL80	Mixture of 80% perfluorinated phosphinic / phosphoric acids and 20% water	Clariant
Plurasolv® IPL	Isopropyl lactate	Plurac
Rhodacal® 70/B	70% Calcium dodecyl benzene sulfonate	Rhodia
Rhodacal® 60/BE	60 % Calcium dodecyl benzene sulfonate	Rhodia
Rhodorsil® 454	Mixture of polydimethylsiloxanes and silica	Rhodia
Solvesso 200	Aromatic hydrocarbon mixture	Exxon Chemicals
Ukanil® 2507	Castor oil ethoxylate	Uniqema
Witconol® 1095	Technical methyl decanoate	Witco Corp.

**Examples 1 to 3**

EC formulations are prepared containing:

Component	Function	Concentration (g/L)		
		Example		
		1	2	3
Picolinafen	Active Ingredient (a)	50	50	50
MCPA 2-EH	Active Ingredient (b)	780	780	780
Atlox 4855 B	Emulsifying system (c)+(d)	100	100	100
Fluowet PL 80	Defoamer (f)	0.5	0.5	0.5
Solvesso 200	Solvent (e)	To 1 L	-	-
Purasolv IPL	Solvent (e)	-	to 1 L	-
Exxsol D 110	Solvent (e)	-	-	To 1 L

**Foaming Behavior**

- 5 The foaming behavior is assessed according to CIPAC Method MT 47 and is shown in the following Table I.

**Table I:** Foaming behavior

Test	Example 1	Example 2	Example 3
Persistent Foaming (2 % in CIPAC Standard Water C) after 10 s	7.5 mL	10 mL	2.5 mL
after 1 minutes	0 mL	0 mL	0 mL
after 3 minutes	0 mL	0 mL	0 mL
after 12 minutes	0 mL	0 mL	0 mL

- 10 The properties of the EC formulations have been evaluated according to the following CIPAC procedures:

(A) Emulsion Characteristics (CIPAC MT 36)

- 5 5 mL of the respective EC are mixed with water (342 ppm hardness) to give 100 mL of an aqueous emulsion. The stability of the emulsion is assessed in terms of oil or cream which separates while the emulsion is allowed to stand undisturbed for 24 hours at 30 °C. The ability to re-emulsify at the end of the 24 hours period is also determined

(B) Low Temperature Stability (CIPAC MT 39)

- 10 A sample of the respective EC is maintained for 1 hour at 0 °C and the volume of any separated solid or oily matter is then recorded. The sample is stored for 7 days, and then allowed to remain undisturbed at ambient temperature for 3 hours. Subsequently, the sample is centrifuged and any solid matter and the volume thereof is recorded.
- 15 The spray dilutions of the formulations proved to be homogeneous emulsions which were entirely stable over at least 2 hours at 30° C (CIPAC Method MT 36). The formulations exposed no precipitation of solid material when they where stored over a period of 7 days at 0° C (CIPAC Method MT 39).

20

**Examples 4 to 6**

EC formulations are prepared containing:

Component	Function	Concentration (g/L) Example		
		4	5	6
Picolinafen	Active Ingredient (a)	50	50	50
MCPA 2-EH	Active Ingredient (b)	780	780	780
Ukanil 2507	Nonionic surfactant (c)	60	-	50
Rhodacal 60/BE	Anionic surfactant (d)	60	-	-
Rhodacal 70/B	Anionic surfactant (d)	-	-	50
Atlox 4855 B	Emulsifying system (c)+(d)	-	100	-
Rhodorsil 454	Defoamer (f)	-	0.5	-
Exxsol D 110	Solvent (e)	to 1 L	-	-
Solvesso 200	Solvent (e)	-	to 1 L	-
Witconol 1095	Solvent (e)	-	-	to 1 L

The properties of the EC formulations have been evaluated according to the following CIPAC or OECD procedures:

5

(C) pH 1% in water (CIPAC MT 75)

The pH of a 1 % dilution of the formulation in demineralized water is determined at 20 °C by means of a pH meter and a glass electrode.

10 (D) Density (OECD Guideline 109)

The density of the respective EC is measured at 20 °C by means of an oscillating density meter.

15 The characteristics of the EC formulations of examples 4 to 6 obtained with the methods described hereinabove are shown in the following Table II.

Table II: Characteristics of the EC formulations

Characteristic	Test Method	Example 4	Example 5	Example 6
Emulsion Characteristics - after 30 min - after 2 h - after 24 h - re-emulsification - final emulsion stability	CIPAC MT 36	uniform uniform uniform uniform uniform	uniform uniform uniform uniform uniform	uniform uniform uniform uniform uniform
Low temperature stability at 0° C	CIPAC MT 39	no separated material	no separated material	no separated material
pH 1 % in water	CIPAC MT 75	4.4	not det.	not det.
Density	OECD 109	1.048 g/mL	1.066 g/mL	1.052 g/mL

The foaming behavior of all EC formulations had been assessed  
 5 according to CIPAC Method MT 47. There was less than 20 ml of  
 persistent foam upon dilution with water (1 to 2 %) and 30 inversions in a  
 100 ml graduated cylinder filled with 100 ml water.

**Examples 7 to 9**

10 EC formulations are prepared containing:



Component	Function	Concentration (g/L)		
		Example		
		7	8	9
Picolinafen	Active Ingredient (a)	50	100	100
2,4-D 2-EH	Active Ingredient (b)	422	844	844
Ukanil 2507	Nonionic surfactant (c)	60	60	60
Rhodacal 60/BE	Anionic surfactant (d)	60	60	60
Agsolex BLO	Solvent (e)	to 1 L	to 1 L	-
Agsolex1	Solvent (e)	-	-	to 1 L

The characteristics of the EC formulations of examples 7 to 9 obtained with the methods described hereinabove are shown in the following Table

5 III.

Table III: Characteristics of the EC formulations

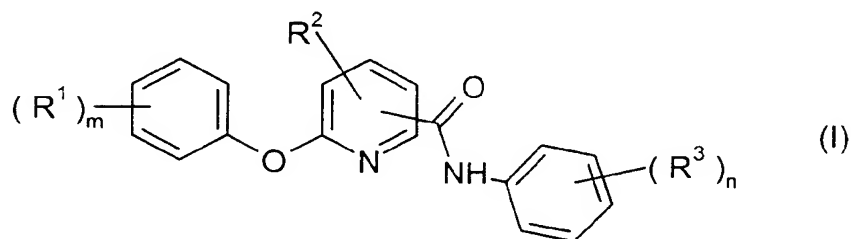
Characteristic	Test Method	Example 7	Example 8	Example 9
Emulsion Characteristics	CIPAC MT 36			
- after 30 minutes		uniform	uniform	uniform
- after 2 hours		uniform	uniform	uniform
- after 24 hours		uniform	uniform	uniform
- re-emulsification		uniform	uniform	0.5 ml oil
- final emulsion stability		uniform	uniform	uniform
Low temperature stability at 0° C	CIPAC MT 39	no separated material	no separated material	no separated material
pH 1 % in water	CIPAC MT 75	6.4	6.2	not det.
Density	OECD 109	1.133 g/mL	1.141 g/mL	not det.

The spray dilutions (emulsions) of examples 7 to 9 are stable despite the presence of water-miscible substances (N-methylpyrrolidone,  $\gamma$ -butyrolactone). The ingredients have a good environmental profile. The foaming behavior of all EC formulations had been assessed according to  
5 CIPAC Method MT 47. There was less than 20 ml of persistent foam upon dilution with water (1 to 2 %) and 30 inversions in a 100 ml graduated cylinder filled with 100 ml water.

WHAT IS CLAIMED IS:

- 5           1.     A non-aqueous, emulsifiable concentrate formulation (EC) for herbicidal crop protection active compounds which consists essentially of
- (a) 25 to 150 g/L of at least one fluorinated herbicidal compound;
- (b) 400 to 900 g/L of one or more herbicidal alkyl phenoxyalkanoates,
- 10   (c) 10 to 100 g/L of at least one non-ionic surfactant,
- (d) 10 to 100 g/L of at least one benzene sulfonate,
- (e) 50 to 600 g/L of one or more solvent selected from the group consisting of aliphatic or aromatic hydrocarbons, methylated plant oils and water-miscible polar aprotic organic solvents, and
- 15   (f) optionally, up to 5 g/L of a defoamer.

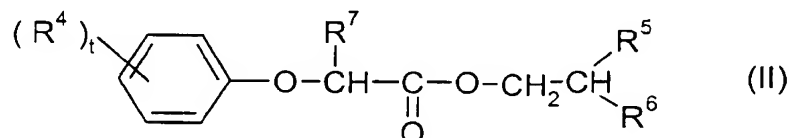
2.     A non-aqueous, emulsifiable concentrate formulation (EC) of Claim 1 wherein the fluorinated herbicidal compound (a) is of the formula
- I



- 20   in which
- R<sup>1</sup> and R<sup>3</sup> each independently represent a fluorine atom or a fluoroalkyl group;
- R<sup>2</sup> represents a hydrogen atom or an optionally substituted alkyl or alkoxy group;
- 25   m and n each independently represent an integer from 1 to 2.

5                   3.     An emulsifiable concentration formulation Claim 1 wherein  
said fluorinated herbicidal compound (a) is N-(4-fluorophenyl)-2-(3- $\alpha,\alpha,\alpha$ -  
trifluoromethylphenoxy)-6-pyridinecarboxamide.

                  4.     An emulsifiable concentration formulation in accordance with  
10    Claim 1 wherein the herbicidal allaryl phenoxyalkanoate (b) is an alkyl  
phenoxy acetate of formula II



wherein

R<sup>4</sup> each independently represents a halogen atom or a C<sub>1-6</sub> alkyl group,  
15    R<sup>5</sup> and R<sup>6</sup> each independently represent a C<sub>1-6</sub> alkyl group,  
R<sup>7</sup> represents a hydrogen atom or a methyl group, and  
t represents an integer from 1 to 3.

                  5.     An emulsifiable concentration formulation Claim 4 wherein  
the alkyl phenoxy acetate (b) is selected from the group consisting of 2-  
20    ethylhexyl (4-chloro-2-methylphenoxy)-acetate, 2-ethylhexyl (2,4-  
dichlorophenoxy)-acetate and 2-ethylhexyl 2-(4-chloro-2-methylphenoxy)-  
propionate or a mixture thereof.

                  6.     An emulsifiable concentration formulation Claim 1 wherein  
said non-ionic surfactant (c) is an ethoxylated castor oil.

25                   7.     An emulsifiable concentration formulation Claim 1 wherein  
said benzene sulfonate (d) is a sodium or calcium alkyl-benzene  
sulfonate.

                  8.     An emulsifiable concentration formulation Claim 1 which  
consists essentially of

- (a) 30 to 125 g/L of at least one fluorinated herbicidal compound of formula I;
  - (b) 700 to 875 g/L of one or more herbicidal alkyl phenoxyalkanoate of formula II,
  - 5 (c) 20 to 75 g/L of at least one non-ionic surfactant,
  - (d) 20 to 75 g/L of at least one sodium or calcium alkyl-benzene sulfonate,
  - (e) 50 to 200 g/L of one or more solvent selected from the group consisting of aliphatic or aromatic hydrocarbons, methyl C<sub>8-12</sub> carboxylates, N-methylpyrrolidone,  $\gamma$ -butyrolactone and isopropyl
  - 10 lactate; and
  - (f) optionally, up to 2 g/L of at least one defoamer selected from the group consisting of polydimethylsiloxanes and perfluoroalkylphosphonic / perfluoroalkylphosphonic acids:
- 15           9.       A method for the control of undesired weed at a locus which comprises emulsifying the formulation of Claim 1 with water and treating said locus with the obtained diluted aqueous formulation.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/17567

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A01N25/02 A01N43/40 A01N39/02 A01N39/04 //(A01N43/40,  
39:04,39:02)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	EP 1 025 757 A (AMERICAN CYANAMID CO) 9 August 2000 (2000-08-09) page 4, line 34 -page 6, line 31; examples 1-3	1-9
Y	WO 98 48624 A (ISP INVESTMENTS INC) 5 November 1998 (1998-11-05) page 2, paragraph 5 -page 3, paragraph 1 page 5, line 4; table 1	1,4-7,9
Y	GB 1 598 327 A (LILLY INDUSTRIES LTD) 16 September 1981 (1981-09-16) page 1, line 16-24 page 1, line 33-45; examples 1,2	1,4-7,9
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

4 October 2000

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/17567

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 1 586 463 A (SHELL INT RESEARCH) 18 March 1981 (1981-03-18) page 1, line 25 -page 2, line 15 page 3, line 52-63; examples 1-3 -----	1,4-7,9

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/17567

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1025757	A	09-08-2000	NONE	
WO 9848624	A	05-11-1998	US 5834400 A AU 6569698 A	10-11-1998 24-11-1998
GB 1598327	A	16-09-1981	AR 220144 A AU 524585 B AU 3830178 A BR 7804970 A EG 13681 A FR 2399211 A GR 63165 A IL 55171 A IT 1107451 B JP 54035216 A PH 16376 A TR 20105 A	15-10-1980 23-09-1982 31-01-1980 24-04-1979 30-09-1982 02-03-1979 26-09-1979 30-01-1981 25-11-1985 15-03-1979 14-09-1983 24-07-1980
GB 1586463	A	18-03-1981	AT 358864 B AT 568077 A AU 511681 B AU 2751277 A BE 857377 A BR 7705038 A CA 1099127 A CS 196217 B DD 131122 A DE 2734684 A DK 344177 A FI 772334 A FR 2360251 A GR 64046 A IT 1085429 B NL 7708417 A NO 772714 A NZ 184792 A PL 200001 A PT 66870 A, B RO 72715 A SE 7708783 A SU 730270 A TR 19742 A ZA 7704630 A	10-10-1980 15-02-1980 28-08-1980 08-02-1979 01-02-1978 02-05-1978 14-04-1981 31-03-1980 07-06-1978 09-02-1978 03-02-1978 03-02-1978 03-03-1978 19-01-1980 28-05-1985 06-02-1978 03-02-1978 08-05-1980 28-03-1978 01-09-1977 09-09-1982 03-02-1978 25-04-1980 25-10-1979 28-06-1978